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STABLE ISOTOPES OF SULFUR IN SUBTERRANEAN WATERS (A SURVEY OF THE LITERATURE)

[Stabil'nyye izotopy sery v podzemnykh vodakh (literaturnyy obzor)]

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STABLE SULFUR ISOTOPES IN SUBTERRANEAN WATERS (A SURVEY OF THE LITERATURE)

A. L. Rabinovich*

ABSTRACT. In the article, reports on the isotope composition of the sulfur which forms a part of the different compounds dissolved in subterranean waters is examined by classes according to the origin of the waters. All of the values are given in recalculation for δS^{34} (‰). The plus sign in front of the value δS^{34} indicates the enrichment of the sample with the heavy isotope S^{34} in comparison with the sulfur of meteorite troilite; the minus sign indicates enrichment of the sample with the light isotope S^{32}.

The Isotope Composition of Sulfate and Sulfide Sulfur in Stratal Waters of Petroleum and Gas Deposits

The isotope composition of sulfur of stratal water sulfates has been studied in connection with the problem of the origin of petroleum (specifically, the sulfur of petroleums), and of hydrogen sulfide in casing-head and fuel gases.

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It has been shown that petroleum and sulfates of the enclosing sedimentary rocks have a common source of sulfur, in all probability the sulfates of basins of sediment accumulation. The isotope composition of the sulfur of petroleums in this case may be similar to the composition of the sulfur of the sulfates of the fossil seas. Where petroleum formed in the closed seas or lagoons and where a number of processes led to a change in the δS^{34} value, the isotope composition of petroleum sulfur is different from the original sulfate (Yeremenko, 1963a, 1963b; Pankina, 1966, 1967).

The sulfates of the stratal waters are the source of sulfur in casing-head petroleum and fuel gases. Hydrogen sulfide forms during bacterial sulfate reduction. This process occurs most intensively in zones of direct contact of petroleum and water (Pankina, et al., 1964), and in the strata that are of younger geological age. In the more ancient strata, the process is weaker and is often not found at all (Yeremenko, et al., 1963c).

Hydrogen sulfide with varying isotope composition forms, depending on the course of the process of microbiological reduction of the sulfates. Thus, the enrichment of hydrogen sulfide with S^{32} occurs in the presence of a significant source of sulfate and with continuous replenishment of sulfate losses in the process of sulfate reduction. With equality of the rates of supply of sulfates and sulfate reduction, the isotope composition of the sulfur of sulfates and hydrogen sulfide may be practically identical. During prolonged bacterial reduction of sulfates in strata with insufficient supply, the first fractions of hydrogen sulfide will be enriched with S^{32}, while the subsequent ones will be impoverished (Pankina, 1964; Pankina, et al., 1964). The δS^{34} value of sulfates of stratal waters varies from -16.0 to +30.7‰ (Anger, et al., 1962; Yeremenko, et al., 1963a, 1963b, 1963c; Petrenko, 1962); while the δS^{34} value of hydrogen sulfide sulfur dissolved in these waters or forming a component of the natural gases ranges from -22.4 to +25.2‰ (Thode, et al., 1949; Rankama, 1956; Anger, et al, 1962); e.g., a general sulfur enrichment of the hydrogen sulfide with the light isotope is

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observed in comparison with the sulfate sulfur in the course of the process of bacterial reduction of the latter.

The Isotope Composition of Sulfate and Sulfide Sulfur in Mineral Waters

A study of the isotope composition of the sulfur of sulfates and sulfides in subterranean waters of certain regions of the Precaucasians was undertaken to obtain additional data on their origin. It was shown that the isotope composition of the sulfur of sulfates of subterranean waters of certain regions of the Precaucasus is similar to the isotope composition of sulfur of the sulfates of the water-enclosing rock. At the same time, the experiments showed that fractioning of the sulfur isotopes does not occur during the solution of sulfates. Hence, a source of sulfates of subterranean waters is primarily the salt deposits of the ancient basins — the evaporites. The secondary sulfites of the argillaceous rocks play an insignificant role in this case.

As in the case of the petroleum deposits, S^{34} enrichment of the sulfur of hydrogen sulfide, which is often in the stratal waters, is due to the significant intensity of the sulfate reducing process and the organic influx of sulfates. Enrichment of hydrogen sulfide with the light isotope S^{32} is explained by the retarded tempo of microbial reduction of the sulfates.

Enrichment of the sulfate sulfur or certain stratal waters with the light isotope S^{32} is due to the participation of surface waters in their formation and to the dissolution of the secondary sulfates. It is assumed that the secondary sulfates form during the oxidation of the "light" sulfides. Thus, for example, the isotope composition of sulfur compounds of the Caucasian mineral waters built up under the effect of sulfates of the water-enclosing rocks and the connate and surface waters, on the one hand, and the bacterial process of sulfate reduction, on the other. The value of δS^{34} for sulfates of the Caucasian mineral waters varies from +0.7 to +41.0%, and for

δS^{34} for hydrogen sulfide sulfer — from -25.3 to + 20.9% (Pankina, et al., 1966).

The values of δS^{34} of sulfur of sulfates of four hot springs (up to +54° C) and a cold (up to +8° C) sulfur spring in the Rocky Mountains of Canada vary from +15 to +20%; δS^{34} of hydrogen sulfide sulfur proved to be near 0% (Sasaki, et al., 1966); δS^{34} of sulfur formed in water of one of the springs of Calabria (Italy) is 26% (Ancarani-Rossiello, et al., 1963). In both cases, enrichment with the light isotope is related to bacterial activity.

The isotope composition of sulfate sulfur of eight Tyan'-Shan' (USSR) hot nitrogen springs fluctuates from +6.0 to +17.4% (V. I. Vinogradov, 1964a). There are vadose waters of deep circulation with a temperature of 25 - 58° C, and have certain signs of metal-bearing hydrothermal solutions.

The isotope composition of sulfur of sulfates of the vadose waters forms under the influence of sulfates of the ancient seas, sulfur of the secondary sulfates formed as the result of sedimentary sulfides with lightened sulfur, and also as the result of bacterial reduction processes (V. I. Vinogradov, 1964a, 1967; Chukhrov, et al., 1967).

The primary source of the sulfate of the soils in the ground waters of certain areas may be sedimentary deposits with varying proportions of sulfur of sulfates of marine origin (including the sulfates of the evaporites) and sulfur of sedimentary sulfides, which form sulfates upon oxidation (Chukrov, et al., 1967). /108

The Isotope Composition of the Sulfur of Sulfates in Mine and Shaft Waters

The sulfate ions are often the basic component of mine and shaft waters. But sulfur is primarily encountered in the form of sulfides in the surrounding minerals. Atmospheric oxygen and

microorganisms convert the sulfide sulfur into the sulfate form. Microbiological activity often plays a significant role in the processes of sulfide oxidation (Ivanov, et al., 1958, Lyalikova, 1960, 1961; Nazarova, et al., 1967).

The process of sulfide oxidation occurs much more rapidly under the effect of bacteria than the purely chemical oxidation, and terminates after sterilization of the ore or coal with pyrite (Posokhov, 1967). Oxidation of sulfur and its derivatives in the zone of hypergenesis is basically due to microbiological processes; the processes of chemical oxidation play a much smaller role (Mekhtiyeva, 1964). During the oxidation of sulfur and sulfide as the result of bacterial vital activity, the process of fractioning of the sulfur isotope occurs, to one degree or another (Mekhtiyeva, 1964; Mekhtiyeva, et al., al., 1964, 1966).

The effect of other factors on fractioning the isotopes of sulfur in an aqueous medium are discussed by a number of authors. Thus, laboratory experiments on the oxidation of sulfides demonstrated the absence of isotope migration between the sulfides and sulfur in a different valent state (Vinogradov, A. P., et al., 1964).

At the same time, it is assumed that the solution and transport of sulfates in solution may be accompanied by fractioning as the result of reactions of migration or the kinetic isotope effect, which is the greater, the more soluble the sulfate. Fractioning probably occurs during hydrolysis of sulfates ($FeSO_4$) and aging of the "oxide hydrosulfates" of the same iron (Vinogradov, V. I., 1963).

Measurement of the δS^{34} values at a number of objects demonstrated that sulfur of a sulfate formed from sulfide usually has the same δS^{34} value as the sulfide, or differs extremely little (Vinogradov, V. I., 1963, 1967; Gavrikova, et al., 1967; Deshou, 1964).

The isotope composition of sulfate sulfur of mine waters of three mines (Canada, USSR, and Japan) ranges from -8.9 to +22.8‰ (Vinogradov, V. I., 1963; Deshou, 1964; Sakai, 1957).

The Isotope Composition of Sulfur in Waters of Volcanic Regions

Three forms of sulfur are ordinarily encountered in waters of regions of volcanic activity: sulfide, elementary, and sulfate.

Elementary sulfur forms in crater lakes and springs of the geothermal regions under the effect of sulfur dioxide and hydrogen sulfide (Vinogradov, V. I., 1965) or during the oxidation of hydrogen sulfide by atmospheric oxygen (Rafter, et al., 1960; Grinenko, et al., 1967).

The sulfur of sulfates is a product of hydrogen sulfide oxidation by atmospheric oxygen, of the oxidation of elementary sulfur, and the result of an admixture of deep SO_3 (Rafter et al., 1960; Grinenko, et al., 1967). Moreover, the sulfates appear as the result of washout of the soluble salts from the walls by atmospheric precipitation (Vinogradov, V. I., 1965) and in the course of bacterial oxidation (Rafter, et al., 1960; Ivanov, et al., 1968). /109

All of the diversity of variation of the isotope composition of sulfur and its compounds in the volcanic and geothermal waters is explained by the oxidative-reducing and biochemical reactions occurring in the zone of volcanic activity.

The study of the isotope composition of various kinds of sulfur shows that volcanic sulfur is not of juvenile origin; the juvenile sulfur plays a subordinate role (Vinogradov, V. I., 1964b). S^{34} enrichment of sulfate sulfur, in comparison with sulfide and elementary sulfur, and the similarity of its isotope composition to the isotope composition of sulfur of the sulfates of sedimentary origin and sulfur of oceanic sulfate shows that "subterranean waters, including modern and fossil sea waters, are involved" in the volcanic process (Ozerova, et al., 1967). The formation of sulfate enriched S^{34} is due to sulfide oxidation (Ibid.). The oxidation of the sulfide forms of sulfur in fumarole fields of active volcanoes

partially occurs with the participation of microorganisms (Ivanov, et al., 1968).

The significant lightening of hydrogen sulfide sulfur in springs (in regions of volcanic activity) is due to the activity of the sulfate-reducing bacteria (Rafter, et al., 1960).

Hydrogen sulfide in the water of crater lakes precipitates the so-called chalcophil elements (Zn, Fe, As, Cu, etc.). In this case, iron may play the role of a coprecipitant for the elements in the water in small concentrations. Naturally, the ore elements thereby concentrated have a "lightened" isotope composition of sulfur, as does the original hydrogen sulfide (Vinogradov, V. I., 1965).

The isotope composition of hydrogen sulfide and the sulfides varies in a range of 20%, with an equally probable deviation to both sides of δS^{34} of the sulfur of meteorite troilite. The δS^{34} value of elementary sulfur varies from +10 to -15%. The oxide forms of sulfur are basically strongly enriched with S^{34} — up to +27.8% (Vinogradov, V. I., 1966; Sakai, 1957; Kaplan, et al., 1960; Rafter, et al., 1958).

Conclusions

1. δS^{34} values of sulfur of sulfates of stratal petroleum waters vary from -16.0 to +30.7%; δS^{34} values of sulfide sulfur range from -22.4 to +25.2%. The reason for the significant changeability of the δS^{34} values is processes of microbiological sulfate reduction.

2. The δS^{34} values for sulfur of sulfates in waters of mineral springs ranges from +0.7 to +41.0%, while δS^{34} for sulfur of sulfides ranges from -25.3 to +20.9%. The cause of the significant scatter in the values of δS^{34} is processes of microbial sulfate reduction and the addition of sulfur with varying isotope composition from the sedimentary rocks.

3. The isotope composition of sulfur of sulfates of mine and shaft waters depends on the isotope composition of sulfur of the oxidizing sulfides and the isotope composition of sulfates introduced from outside. The process of formation of the isotope composition of the sulfates of shaft waters may be complicated by fractioning of sulfur isotope due to microbiological oxidation of sulfides.

4. The oxide forms of sulfur are usually enriched with respect to S^{34} in waters of volcanic regions (δS^{34} up to +27.8‰) elementary sulfur — basically enriched with S^{32} (δS^{34} fluctuates from +10 to -15‰); sulfide sulfur — varies with respect to both isotopes (δS^{34} fluctuates from -10 to +10‰). The biochemical oxidative-reduction processes are widespread in regions of volcanic activity.

In the light of the examined data, fractioning of the sulfur isotopes during the microbiological reducing processes is unquestionably one of the determinative factors in the formation of the isotope composition of sulfur compounds in subterranean waters.

The study of the effect of processes of oxidation on the isotope composition of sulfur (both microbiological processes and chemical processes) does not at present give a determinable result.

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